# Synthesis of 1,4-Bis(allyloxy)- and 1,4-Bis(2,3-dibromopropoxy)-2,3,5,6-tetrachlorobenzene

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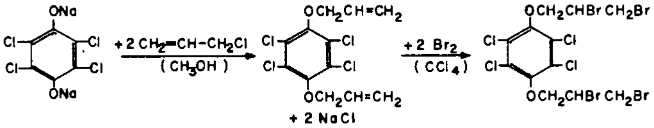
**The synthesis of 1,4-bis(allyloxy)-2,3,5,6-tetrachlorobenzene (diallyl ether of tetrachlorohydroquinone) was accomplished in 60% yield by reaction of tetrachlorohydroquinone with sodium methoxide and allyl chloride in methanol. The bromination of 1,4-bis(allyloxy)-2,3,5,6-tetrachlorobenzene afforded 1,4-bis(2,3-dibromopropoxy)-2,3,5,6-tetrachlorobenzene in 81.5% yield. The infrared spectra of the compounds are discussed briefly.**

NONE of the allyl ethers of chlorinated hydroquinones have been described in the literature. The synthesis of the diallyl ether of tetrachlorohydroquinone [1,4-bis(allyloxy)-2,3,5,6-tetrachlorobenzene] (II) has now been accomplished. The method used consisted in treating tetrachlorohydroquinone with sodium methoxide followed by addition of allyl chloride using methanol as reaction medium. Product yield was 60%. When sodium hydroxide was used as the base and an acetone-water mixture as a medium, the reaction resulted in about 2% yield of product. The bromination of 1,4-bis(allyloxy)-2,3,5,6-tetrachlorobenzene in carbon tetrachloride resulted in 81.5% yield of 1,4 - bis(2,3 - dibromopropoxy) - 2,3,5,6 - tetrachlorobenzene (III).

The infrared absorption bands are reported in the experimental section. The spectrum of 1,4-bis(allyloxy)-2,3,5,6-tetrachlorobenzene (II) does not exhibit the four characteristic frequencies of the aromatic ring skeletal vibrations (*1*) in the 1650 to 1450 $cm.^{-1}$ region. It shows only two weak bands—a band at 1644 $cm.^{-1}$, probably arising from ethylenic C=C stretching vibration; and a band at 1468 $cm.^{-1}$, assignable to methylene bending vibration (*1*). The strong bands at 980 and 936 $cm.^{-1}$ disappeared upon bromination of the compound. This suggests that these bands are associated with the ethylenic double bonds; they may be attributed to out-of-plane ethylenic C—H bending vibrations (*1*). The lower frequency band has an overtone at 1885 $cm.^{-1}$ (*2*). The four bands arising from skeletal stretching modes of the aromatic C—C bond appear at 1645 $cm.^{-1}$, 1630 $cm.^{-1}$, 1588 $cm.^{-1}$, and 1455 $cm.^{-1}$ in the spectrum of 1,4-bis(2,3-dibromopropoxy)-2,3,5,6-tetrachlorobenzene (III). The low frequency band may also arise from methylene bending vibrations (*1*). Furthermore, the brominated compound shows four bands in the frequency range 670 to 590 $cm.^{-1}$; these bands are very likely caused by C—Br stretching vibrations (*1*).



I II III

## EXPERIMENTAL

The spectra were recorded on a Perkin Elmer infrared spectrophotometer Model 221 equipped with sodium chloride prism-grating interchange (potassium bromide pellets technique, 0.5% by weight of compound).

**1,4-Bis(allyloxy)-2,3,5,6-tetrachlorobenzene (II).** Tetrachlorohydroquinone (62.0 grams; 0.25 mole) was dissolved in absolute methanol (270 ml.) contained in a 1-liter, round-bottomed flask equipped with a reflux condenser, pressure equalizing addition funnel, thermometer, and a mechanical stirrer.

To the vigorously stirred solution maintained at 30° C. under a nitrogen atmosphere was added dropwise over a 10-minute period a solution of sodium methoxide (14.5 grams assaying 95%; 0.255 mole) dissolved in methanol (105 ml.). Allyl chloride (23.0 grams; 0.3 mole) was added during 15 minutes, while the temperature was maintained at 30° to 35° C. After being refluxed for 20 hours, the reaction mixture was cooled to 30° C. and treated with a second portion of sodium methoxide (14.5 grams; 0.255 mole), followed by addition of allyl chloride (23.0 grams; 0.3 mole) in a manner similar to that described above. The reaction mixture, a brown-colored suspension, was cooled to +5° C. and filtered. The crystalline precipitate was stirred with two portions of 250 ml. of water and once with 250 ml. of 0.4% aqueous solution of sodium hydroxide. The crystals were washed with 250 ml. of water and sucked dry. Drying under reduced pressure at 50° to 60° C. gave 49.2 grams (60% yield) of 1,4-bis(allyloxy)-2,3,5,6-tetrachlorobenzene (diallyl ether of tetrachlorohydroquinone), m.p. 124°–125° C. After crystallization from methanol, the compound melted at 126.6°–127.5° C. Anal. Calcd. for $C_{12}H_{10}Cl_4O_2$: C, 43.95; H, 3.05; Cl, 43.25. Found: C, 44.11; H, 3.39; Cl, 42.70. The infrared spectrum showed absorption maxima at 3091 cm.$^{-1}$ (m), 3022 cm.$^{-1}$ (m), 2989 cm.$^{-1}$ (m), 2950 cm.$^{-1}$ (m), 2895 cm.$^{-1}$ (m), 1885 cm.$^{-1}$ (w), 1644 cm.$^{-1}$ (w), 1468 cm.$^{-1}$ (w), 1433 cm.$^{-1}$ (m), 1408 cm.$^{-1}$ (vs), 1370 cm.$^{-1}$ (s), 1330 cm.$^{-1}$ (m, shoulder), 1285 cm.$^{-1}$ (m), 1238 cm.$^{-1}$ (w), 1222 cm.$^{-1}$ (w), 1168 cm.$^{-1}$ (m), 1153 cm.$^{-1}$ (w), 992 cm.$^{-1}$ (s), 980 cm.$^{-1}$ (vs), 963 cm.$^{-1}$ (vs), 936 cm.$^{-1}$ (s), 865 cm.$^{-1}$ (s), 714 cm.$^{-1}$ (s) and 689 cm.$^{-1}$ (m).

**1,4 - Bis(2,3 - dibromopropoxy) - 2,3,5,6 - tetrachlorobenzene (III).** 1,4-Bis(allyloxy)-2,3,5,6-tetrachlorobenzene (32.8 grams; 0.1 mole) was dissolved in boiling carbon tetrachloride (130 ml.) contained in a 300-ml., round-bottomed flask equipped with a thermometer, an addition funnel, a mechanical stirrer, and a reflux condenser. To the vigorously stirred solution was added over a 25-minute period a solution of bromine (32.6 grams; 0.204 mole) in carbon tetrachloride, while the temperature was maintained at 78°–80° C. After the addition was completed, stirring was continued for 15 minutes. Filtration and crystallization of the precipitate from carbon tetrachloride gave 52.8 grams (81.5% yield) of 1,4-bis(2,3-dibromopropoxy)-2,3,5,6-tetrachlorobenzene, m.p. 172.0°–172.8° C. Anal. Calcd. for $C_{12}H_{10}Br_4Cl_4O_2$: C, 22.30; H, 1.55; Cl, 21.90; Br, 49.30. Found: C, 22.11; H, 1.70; Cl, 21.55; Br, 48.84. The infrared spectrum showed absorption maxima at 2925 cm.$^{-1}$ (m), 2855 cm.$^{-1}$ (m), 1930 cm.$^{-1}$ (w), 1690 cm.$^{-1}$ (m, shoulder), 1645 cm.$^{-1}$ (s), 1630 cm.$^{-1}$ (s, shoulder), 1588 cm.$^{-1}$ (m), 1455 cm.$^{-1}$ (m), 1395 cm.$^{-1}$ (m), 1285 cm.$^{-1}$ (s), 1252 cm.$^{-1}$ (s), 1143 cm.$^{-1}$ (s), 1115 cm.$^{-1}$ (s), 1098 cm.$^{-1}$ (m), 1048 cm.$^{-1}$ (m), 1029 cm.$^{-1}$ (m), 1020 cm.$^{-1}$ (m), 992 cm.$^{-1}$ (m, shoulder), 967 cm.$^{-1}$ (m), 948 cm.$^{-1}$ (m, shoulder), 833 cm.$^{-1}$ (m), 771 cm.$^{-1}$ (w), 743 cm.$^{-1}$ (m), 688 cm.$^{-1}$ (m), 670 cm.$^{-1}$ (m), 651 cm.$^{-1}$ (w), 620 cm.$^{-1}$ (w), and 590 cm.$^{-1}$ (w).

## LITERATURE CITED

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# Azomethine Derivatives of β-Ethoxyethylamine

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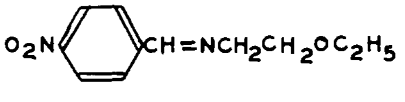
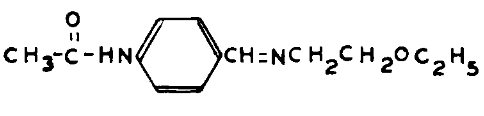
**Syntheses of *N*-(*p*-nitrobenzylidene)-β-ethoxyethylamine and *N*-(*p*-acetamidobenzylidene)-β-ethoxyethylamine are described.**

THE use of β-ethoxyethylamine as an unknown compound in a qualitative organic analysis course requires the existence of known, suitable derivatives. Heilbron (*3*) mentions picrate and picrolonate derivatives only. The literature describes derivatives produced by the reaction of β-ethoxyethylamine with 1,3-bis(*N*-acetylsulfanilyl)urea (*1*), *N,N'*-bis(acetylsulfanilyl)urea, and *N*-(ethoxyethyl)-*N'*-(acetylsulfanilyl)urea (*2*). β-Ethoxyethylamine condenses with *p*-nitrobenzaldehyde and *p*-acetamidobenzaldehyde to give typical azomethines (I and II respectively).



I



II

The preparation and purification of these derivatives are easy and the yields are excellent.